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THE ADDITION OF BENZYNE TO cis- AND trans-1,2-DICHLOROETHYLENE (1)

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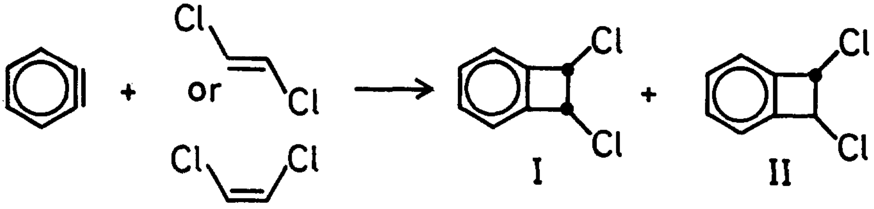
ODDLY ENOUGH, while the chemistry of benzyne has received great attention in recent years (3), and while the stereochemical details of the addition of carbenes to olefins have been subjected to intense scrutiny, little interest has attended the related cycloaddition of benzyne and its stereochemical result. Exceptions are the work of Wasserman and Solodar (5) and the recent report of Tabushi, Oda and Okazaki (6) in which a lack of stereospecificity (7) was observed in the addition of benzyne to substituted enol ethers (8). As our interpretation of similar results differs markedly from that of Tabushi *et al.*, we report here our preliminary findings on the cycloaddition of benzyne and the 1,2-dichloroethylenes.

The two possible products of cycloaddition, *cis*-1,2-dichlorobenzocyclobutene (I) and *trans*-1,2-dichlorobenzocyclobutene (II) were easily separated by gas chromatography (a 2m, 15°/o Dow-Corning 710 silicone oil on 70/80 mesh Anakrom U column operated at 155° with a helium flow of 120 ml/min gave retention times of 10.8 and 4.6 min for I and II respectively). Compound I was isolated as a white solid, mp 90-91° [lit. 91-92°(10)]. The nmr spectrum of I showed a symmetrical multiplet integrating for four protons at τ 2.68 and a two-proton singlet at τ 4.34. The *trans*-compound II was isolated as a colorless liquid and appears to have been previously unknown. High resolution mass spectral analysis (11) established the elemental composition and the nmr spectrum, which showed a four-proton multiplet centered at τ 2.69 and a two-proton singlet at τ 4.74, determined the structure. 1,1-Dichlorobenzocyclobutene seems ruled out by the symmetry of the pattern for the aromatic hydrogens in the nmr and by the chemical shift of the cyclobutyl hydrogens. Given the known (10) stereochemistry of I, there can be no doubt that II is the *trans*-isomer. It is interesting to note that the two dichlorides fit well into the series established by the dibromo and diiodo compounds (12-14). For instance, the trans-isomer is the lower melting in each case and consistently shows its cyclobutyl hydrogens at ca. 0.4 ppm higher field in the nmr.

As II was difficult to separate from a side product of the reaction (15) analysis of the undistilled, crude reaction mixture was made by nmr. Generation of benzyne from benzenediazonium-2-carboxylate hydrochloride (16) in trans-1,2-dichloroethylene led to I and II in the approximate ratio 20/80. Neither temperature, length of heating, dilution, nor use of ethyl iodide as solvent had an appreciable effect on this ratio. When the cycloaddition was to cis-1,2-dichloroethylene the same two products were formed in the ratio 68/32, albeit in much smaller yield. The products were shown to be stable under the reaction conditions and the olefins were not appreciably isomerized during the reaction.



TABLE

OLEFIN	°/oI	°/oII	°/oYIELD	SOLVENT	~T°	HR.	SOURCE
trans (15 equiv.)*	19	81	40	150ml EtCl$_2$**	65	2	HCl***
trans (15 equiv.)	17	83		150ml EtCl$_2$	40	35	HCl
trans (5 equiv.)	20	80		600ml EtCl$_2$	80	2	HCl
trans (15 equiv.)	20	80	32	600ml EtCl$_2$	80	2	HCl
trans (15 equiv.)	16	84		75ml MeCl$_2$	40	24	Carbox.****
trans (15 equiv.)	20	80		75ml EtCl$_2$	55	2	Carbox.
trans (15 equiv.)	19	81		300ml EtI	55	2	HCl
cis (15 equiv.)*	68	32	5	150ml EtCl$_2$	65	2	HCl
cis (15 equiv.)	60	40		300ml EtCl$_2$	80	2	HCl
cis (15 equiv.)	70	30		300ml EtI	65	3	HCl

*average of several runs. **1,2-dichloroethane. ***benzenediazonium-2-carboxylate hydrochloride. ****benzenediazonium-2-carboxylate

As can be seen from the table, our results show substantial but by no means complete equilibration. This is in agreement with the results of Wasserman and Solodar (5) and Tabushi, et al. (6). The latter authors attribute the lack of stereospecificity to triplet benzyne, citing analogy with the reactions of singlet and triplet carbenes. We feel that triplet intermediates do not best explain the results and are certainly not demanded. The confidence now generally placed (17) in an assignment of spin state from stereochemical information in a carbene reaction has only recently become appropriate as reactions of both the singlet and triplet states of some carbenes became known (18-20). Even here doubt will linger until the role of excited diazo compounds is determined. Given the cogent arguments in favor of a singlet ground state for benzyne (21) and the inability to detect benzyne triplets by electron spin resonance (22) it seems unreasonable to postulate triplets in this reaction unless no other good explanation is available.

We feel that the cycloadditions of benzyne are best regarded as analogous to the cycloadditions of 1,1-dichloro-2,2-difluoroethylene studied by Bartlett (23). In the terminology of Woodward and Hoffmann (24, 25) such reactions are 2+2 cycloadditions. A concerted, thermal 2S+2S reaction is therefore forbidden while a concerted 2S+2A cycloaddition is allowed. The latter process would generate trans-benzocyclobutene from cis-olefin and cis-benzocyclobutene from trans-olefin. The experimental result is predominant retention, however, and if a contribution from a concerted 2S+2A process is postulated then a contribution from some correspondingly more stereospecific 2S+2S reaction is also needed. Therefore the best explanation seems to us to be a non-concerted cycloaddition in which some bond rotation occurs before closure of the second bond.

REFERENCES AND NOTES

1. This work was supported by grant GP-7819 from the National Science Foundation to whom we express our appreciation.

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